

Seven-coordinated iron(II) spin-crossover molecule: some learning from iron substitution in the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ solid solutions

Hongfeng Wang^a, Chérif Baldé^b, Arnaud Grosjean^a, Cédric Desplanches^{a,*}, Philippe Guionneau^a and Guillaume Chastanet^{a,*}

^aCNRS, Univ. Bordeaux, ICMCB, UMR 5026, F-33600 Pessac, France.

Email: guillaume.chastanet@icmcb.cnrs.fr; cedric.desplanches@icmcb.cnrs.fr

^bLaboratoire de Chimie et Physique des Matériaux (LCPM) Université de Ziguinchor Bp: 523 Ziguinchor- Sénégal. Fax: (+221) 339916809. Tel (+221) 339916809.

Email: cbalde@univ-zig.sn

Electronic Supplementary Information

Table SI.1: Elemental microanalyses of the solid solution materials $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ [found, % (calcd, %)].

Figure SI.1 Dilution factor obtained as a function of the dilution factor expected for $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$. The full line corresponds to the ideal situation where $x(\text{found}) = x(\text{calculated})$.

Figure SI.2 Room temperature powder X-ray diffraction patterns of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ series.

Table SI.2: Crystal data of $[\text{Mn}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ at 270 K and 120 K.

Table SI.3 : Crystal data of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at room temperature.

Figure SI.3 Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at room temperature. The hydrogen atoms have been omitted for clarity.

Table SI.4: Crystal data of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 250 K and 100 K.

Figure SI.4 Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 250 K. The hydrogen atoms have been omitted for clarity.

Figure SI.5 Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 100 K. The hydrogen atoms have been omitted for clarity.

Table SI.5.: Root-Mean-Square Deviations (RMSD) extracted from pairwise molecular overlays of the complexes studied in the paper, $[\text{A}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]$ with $\text{A} = \text{Mn}, \text{Fe}$ or $\text{Fe}_x\text{Mn}_{1-x}$. The average and the maximum values are reported as calculated by *Mercury*⁴⁰ for room-temperature (RT) and low temperatures (LT), when known. Let's recall that the lower the RMSD values are, the more similar are the molecular shapes. Gray boxes indicate the superimposition drawn in Figure 3.

Table SI.6: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at 250 K.

Table SI.7: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 250 K.

Table SI.8: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 100 K.

Table SI.1 : Elemental microanalyses of the solid solution materials $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$ [found, % (calcd, %)]

x	C	H	N	Fe	Mn
1	50.78(50.89)	5.88(5.78)	17.61(17.45)	14.22(13.92)	-
0.966	50.59(50.89)	5.94(5.78)	17.51(17.46)	13.82 (13.45)	0.49 (0.47)
0.964	49.58(50.89)	5.75(5.78)	16.96(17.46)	14.64(13.42)	0.55(0.49)
0.953	50.29(50.89)	5.76(5.78)	17.21(17.46)	13.98(13.27)	0.69(0.64)
0.949	50.04(50.89)	5.79(5.78)	17.19(17.46)	14.18 (13.21)	0.76 (0.70)
0.930	50.76(50.90)	5.95(5.78)	17.48(17.46)	12.39 (12.95)	0.94 (0.96)
0.912	50.68(50.90)	5.79(5.78)	17.45(17.46)	12.70 (12.70)	1.22 (1.21)
0.892	50.90(50.90)	5.66(5.78)	17.56(17.46)	12.86 (12.42)	1.56 (1.48)
0.867	50.46(50.9)	5.83(5.78)	17.31(17.46)	12.77(12.17)	1.83(1.73)
0.853	51.04(50.90)	5.83(5.78)	17.38(17.46)	12.03 (12.02)	1.91(1.88)
0.832	50.90(50.90)	5.84(5.78)	17.52(17.46)	11.71(11.58)	2.32(2.30)
0.812	50.84(50.90)	5.78(5.78)	17.54(17.46)	11.22(11.31)	2.55(2.58)
0.659	49.31(50.93)	5.64(5.78)	16.84(17.47)	9.24(9.18)	4.77(4.67)
0.550	49.68(50.94)	5.77(5.78)	16.89(17.47)	7.99(7.66)	6.53(6.17)
0.312	50.04(50.97)	5.34(5.78)	16.02(17.48)	4.41(4.35)	9.73(9.43)

Figure SI.1 Dilution factor obtained as a function of the dilution factor expected for $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2] \cdot \text{H}_2\text{O}$. The full line corresponds to the ideal situation where $x(\text{found}) = x(\text{calculated})$.

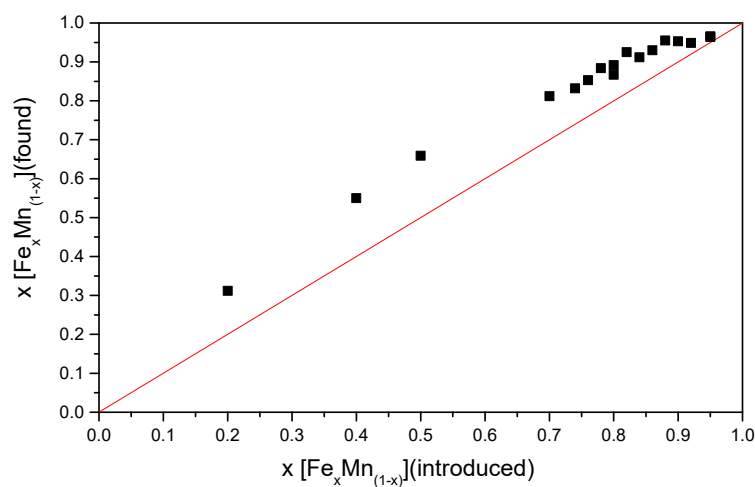


Figure SI.2 Room temperature powder X-ray diffraction patterns of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ series.

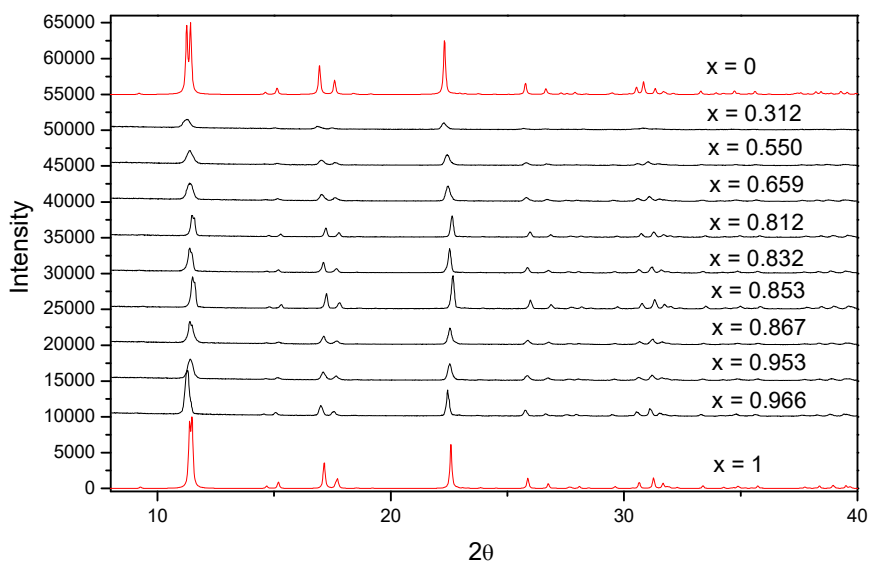


Table SI.2: Crystal data of $[\text{Mn}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ at 270 K and 120 K.

Compound	$[\text{Mn}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$	
	Formula	$\text{C}_{17}\text{H}_{23}\text{MnN}_5\text{O}_3$
λ (Å)	0.71073	0.71073
M_r ($\text{g}\cdot\text{mol}^{-1}$)	400.34	400.34
Colour	brown	brown
Crystal size (mm^3)	$0.45 \times 0.25 \times 0.25$	$0.45 \times 0.25 \times 0.25$
Crystal morphology	cubic	cubic
Temperature (K)	270(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
a (Å)	17.5613(3)	17.093(3)
b (Å)	12.0994(2)	11.990(2)
c (Å)	10.17850(10)	10.330(2)
β (°)	116.5790(10)	113.011(2)
V (Å^3)	1934.18(5)	1893.1(8)
Z	4	4
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.375	1.405
μ (mm^{-1})	0.708	0.724
No. of total reflections	2815	8979
R_{obs}	0.0309	0.0319
$wR2_{\text{obs}}$	0.0839	0.0805
S	1.042	1.082

Table SI.3: Crystal data of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at room temperature.

Compound	$[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$, $x = 0.963 \pm 0.005$
Formula	$\text{C}_{17}\text{H}_{23}\text{Mn}_{0.04}\text{Fe}_{0.96}\text{N}_5\text{O}_3$
λ (Å)	0.71073
M_r ($\text{g}\cdot\text{mol}^{-1}$)	401.22
Colour	dark blue
Crystal size (mm^3)	$0.08 \times 0.08 \times 0.08$
Crystal morphology	cubic
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$C 2/c$
a (Å)	17.3438(8)
b (Å)	12.0771(7)
c (Å)	10.1378(7)
β (°)	116.269(3)
V (Å ³)	1904.19(19)
Z	4
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.400
μ (mm^{-1})	0.818
No. of total reflections	2586
R_{obs}	0.0773
$wR2_{\text{obs}}$	0.1536
S	0.989

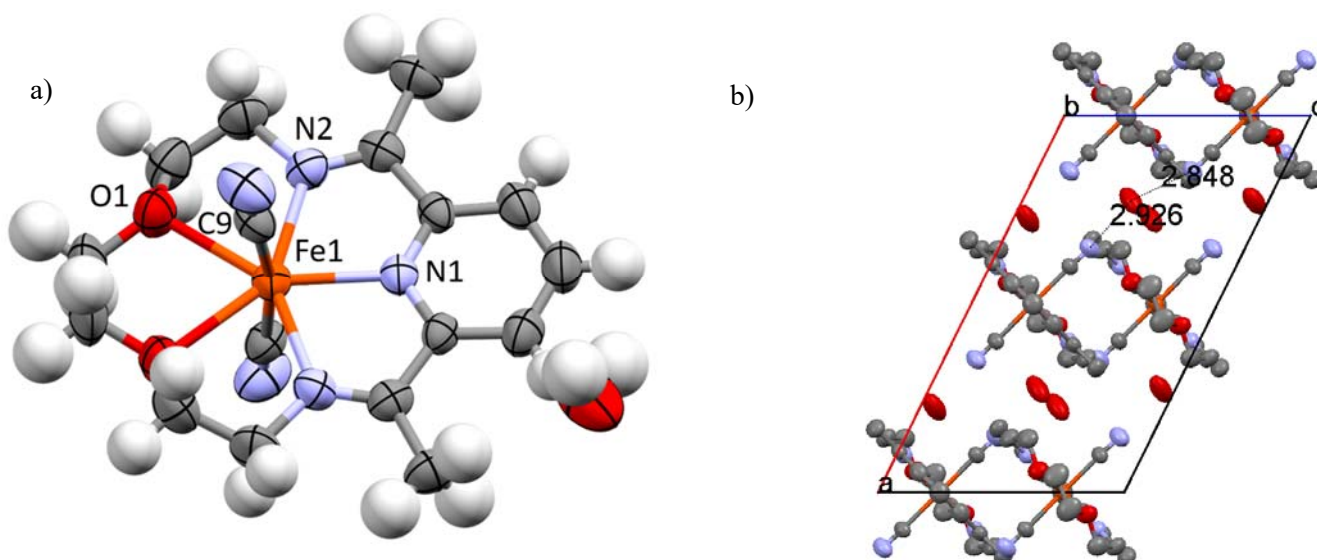
Figure SI.3: Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at room temperature. The hydrogen atoms have been omitted for clarity.

Table SI.4: Crystal data of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638\pm 0.009$ at 250 K and 100 K.

Compound	$[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$, $x = 0.638\pm 0.009$	
Formula	$\text{C}_{17}\text{H}_{23}\text{Mn}_{0.36}\text{Fe}_{0.64}\text{N}_5\text{O}_3$	$\text{C}_{17}\text{H}_{23}\text{Mn}_{0.36}\text{Fe}_{0.64}\text{N}_5\text{O}_3$
λ (Å)	0.71073	0.71073
M_r ($\text{g}\cdot\text{mol}^{-1}$)	400.93	400.93
Colour	dark blue	dark blue
Crystal size (mm^3)	$0.17 \times 0.13 \times 0.13$	$0.17 \times 0.13 \times 0.13$
Crystal morphology	prism	prism
Temperature (K)	250(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	C 2/c	C 2/c
a (Å)	17.3332(4)	17.0528(5)
b (Å)	12.0778(4)	12.0023(4)
c (Å)	10.1168(2)	10.0974(3)
β (°)	116.210(2)	115.880(2)
V (Å^3)	1900.16(9)	1859.40(10)
Z	4	4
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.403	1.433
μ (mm^{-1})	0.820	0.838
No. of total reflections	2164	2116
R_{obs}	0.0589	0.0631
$wR2_{\text{obs}}$	0.1105	0.1208
S	1.061	1.08

Figure SI.4: Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638\pm 0.009$ at 250 K. The hydrogen atoms have been omitted for clarity.

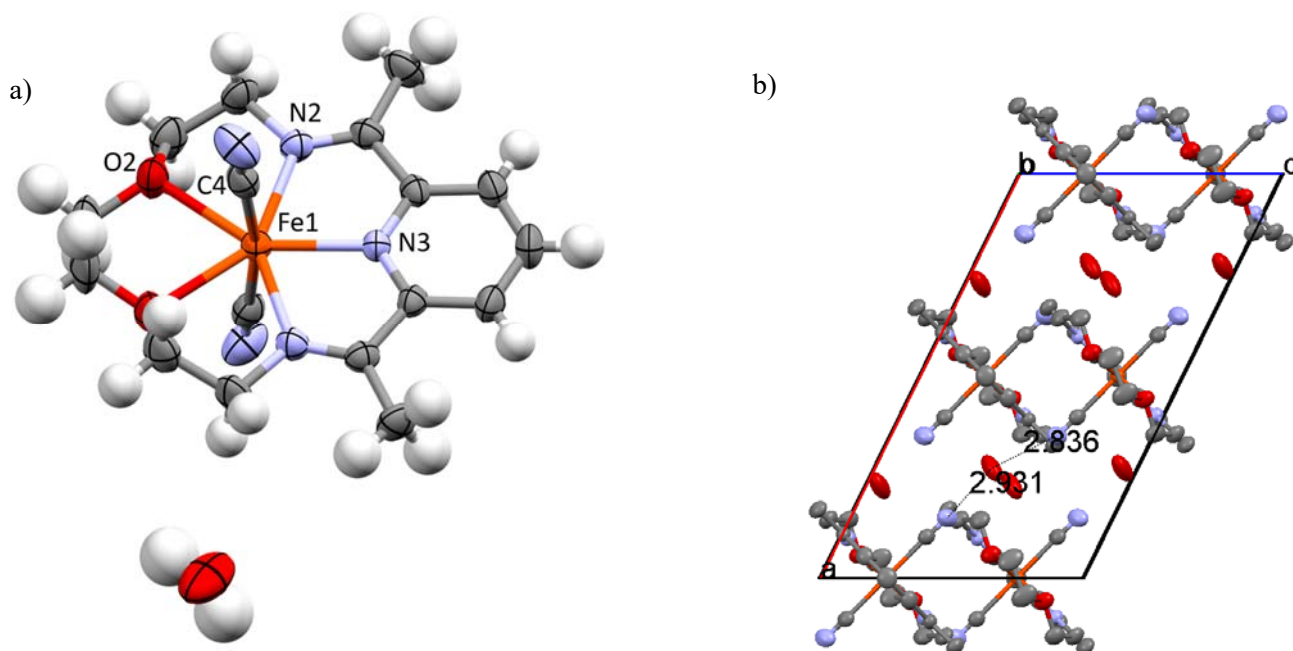


Figure SI.5: Molecular structure (a) and packing (b) of $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638\pm 0.009$ at 100 K. The hydrogen atoms have been omitted for clarity.

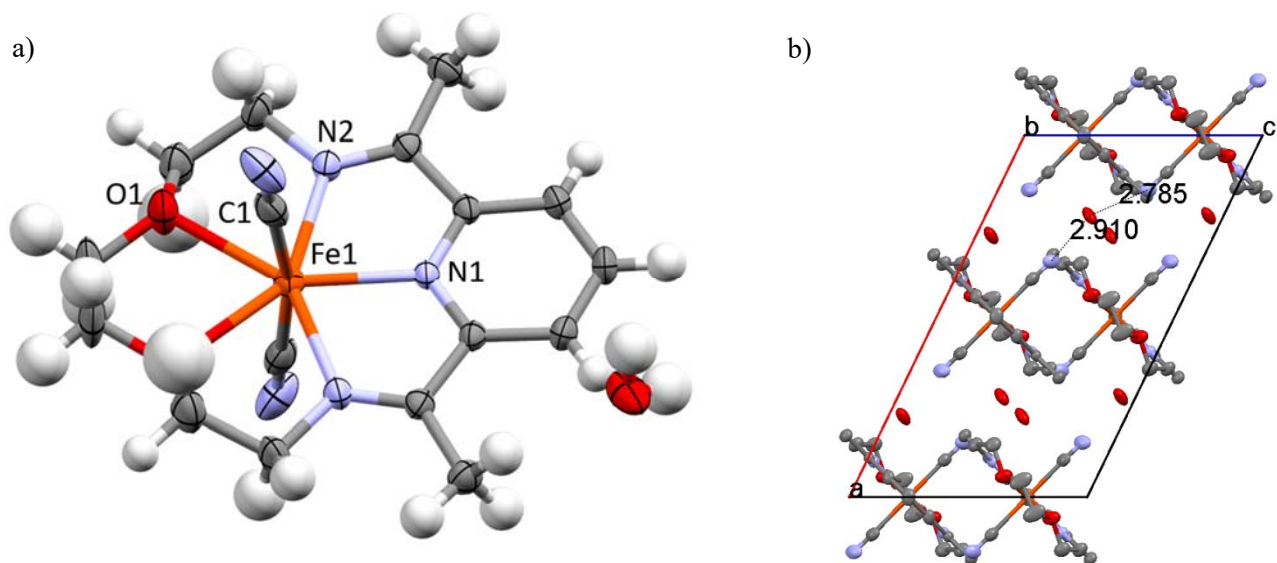


Table SI.5: Root-Mean-Square Deviations (RMSD) extracted from pairwise molecular overlays of the complexes studied in the paper, $[\text{A}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]$ with $\text{A} = \text{Mn}, \text{Fe}$ or $\text{Fe}_x\text{Mn}_{1-x}$. The average and the maximum values are reported as calculated by *Mercury*⁴⁰ for room-temperature (RT) and low temperatures (LT), when known. Let's recall that the lower the RMSD values are, the more similar are the molecular shapes. Gray boxes indicate the superimposition drawn in Figure 3.

<i>RMSD</i> (Å): average (max.)	Mn, RT			
Fe, RT	0.058 (0.131)	Fe, RT		
Fe_{0.64}Mn_{0.36}, RT	0.043 (0.118)	0.021 (0.060)	Fe_{0.64}Mn_{0.36}, RT	
Mn, LT	0.085 (0.267)	0.102 (0.298)	0.103 (0.307)	Mn, LT
Fe_{0.96}Mn_{0.04}, RT	0.060 (0.136)	0.012 (0.018)	0.022 (0.056)	0.101 (0.301)
Fe_{0.64}Mn_{0.36}, LT	0.045 (0.120)	0.019 (0.048)	0.009 (0.056)	0.095 (0.299)

Table SI.6: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.963 \pm 0.005$ at room temperature.

Fe1 — N1	2.122(5)	Fe1 — N2	2.211(3)
Fe1 — O1	2.337(3)	Fe1 — C9	2.174(6)
N1 — Fe1 — N2	72.7(2)	C9 — Fe1 — N1	95.0(2)
N1 — Fe1 — O1	144.5(2)	C9 — Fe1 — N2	92.9(2)
N2 — Fe1 — O1	71.9(1)	C9 — Fe1 — O1	84.2(2)
N2 — Fe1 — N2 ⁱ	145.3(1)	C9 — Fe1 — O1 ⁱ	87.7(2)
N2 — Fe1 — O1 ⁱ	142.7(1)	C9 — Fe1 — N2 ⁱ	90.0(2)
O1 — Fe1 — O1 ⁱ	71.1(1)	C9 — Fe1 — C9 ⁱ	170.0(2)

Table SI.7: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 250 K.

Fe1 — N3	2.143(2)	Fe1 — N2	2.225(2)
Fe1 — O2	2.323(2)	Fe1 — C4	2.224(4)
N3 — Fe1 — N2	72.17(9)	C4 — Fe1 — N3	95.0(1)
N3 — Fe1 — O2	144.05(8)	C4 — Fe1 — N2	92.86(9)
N2 — Fe1 — O2	71.99(7)	C4 — Fe1 — O2	84.07(9)
N2 — Fe1 — N2 ⁱ	144.35(8)	C4 — Fe1 — O2 ⁱ	87.82(9)
N2 — Fe1 — O2 ⁱ	143.60(8)	C4 — Fe1 — N2 ⁱ	90.21(9)
O2 — Fe1 — O2 ⁱ	71.89(7)	C4 — Fe1 — C4 ⁱ	170.0(1)

Table SI.8: Selected geometric parameters (Å, °) for the $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.638 \pm 0.009$ at 100 K.

Fe1 — N1	2.118(4)	Fe1 — N2	2.214(2)
Fe1 — O1	2.329(2)	Fe1 — C1	2.208(4)
N1 — Fe1 — N2	72.6(1)	C1 — Fe1 — N1	95.4(1)
N1 — Fe1 — O1	144.3(1)	C1 — Fe1 — N2	92.9(1)
N2 — Fe1 — O1	71.88(9)	C1 — Fe1 — O1	83.8(1)
N2 — Fe1 — N2 ⁱ	145.13(9)	C1 — Fe1 — O1 ⁱ	87.5(1)
N2 — Fe1 — O1 ⁱ	142.93(9)	C1 — Fe1 — N2 ⁱ	90.3(1)
O1 — Fe1 — O1 ⁱ	71.33(9)	C1 — Fe1 — C1 ⁱ	169.3(1)

Table SI.6: Kinetics performed at 148 K and 190 K after fast cooling at 10 K for the complex $[\text{Fe}_x\text{Mn}_{1-x}(\text{L}_{222}\text{N}_3\text{O}_2)(\text{CN})_2]\cdot\text{H}_2\text{O}$ with $x = 0.949$

